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(54) Title: CONTROLLED RELEASE DEVICE FOR THE PRESERVATION OF WOODEN STRUCTURE PROXIMATE SOIL

(57) Abstract

A method and device are disclosed which prevent the decay and deterioration of wooden objects caused by pests by using a controlled release device. This controlled release device utilizes polymers which incorporate pesticides. In the disclosed method, the controlled release device is placed proximate with the wood of the wooden object. The pesticide is gradually released from the device and absorbed into the wood structure. The pesticide absorbed by the wood creates a barrier or an exclusion zone to penetration by insects. The controlled release device maintains a minimal effective level of pesticide in the barrier or exclusion zone for a predetermined period of time.

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# CONTROLLED RELEASE DEVICE FOR THE PRESERVATION OF WOODEN STRUCTURE PROXIMATE SOIL

## FIELD OF THE INVENTION

The present invention is a controlled release device composed of a polymer, bioactive chemical including at least one fungicide and a binding carrier, effective to prevent or retard wood decay of a wooden object that is in direct contact with soil. As used herein, the term "bioactive" means stimulating an organism, usually in a negative way up to and including death for purposes of a deterrent.

## BACKGROUND OF THE INVENTION

Preserving wood from decay has been recognized as a problem from ancient times. Roman books on architecture had descriptions "of preserving trees after they are cut, what to plaster or anoint them with, of the remedies against their affirmities, and of allotting them their proper place in the building." (See W.C. Hayes, ed., "Extending Wood Pole Life: Solving a $5-billion/year Problem", ELECTRICAL WORLD, 41-47 at 42 (February 1986).

In modern times, the protection of wooden utility poles, railroad ties and fence posts from decay has become a major concern. The decay of such wooden objects has been found to be primarily caused by the action of pests and particularly of fungi, termites, carpenter ants, and other wood invading insects.

The decay caused by fungi is a common and an important source of deterioration of wooden objects by removal or severing of fibers which weakens the wooden object. (See R.A. Zabel et al., The Fungal Associates, Detection, and Fumigant control of Decay in Treated

southern Pine Poles, Final Report EL-2768 for EPRI Research Project 1471-1, State University of New York 1982). Although decay most frequently occurs within 50 centimeters of the ground line, any part of the pole which has a moisture content of above 20% and is in contact with oxygen can harbor decay-producing fungi. The secondary region of decay is the cross-tie intersection area. The fungi feed on wood by extending networks of minute, threadlike strands of single cells (hyphae) through the cracks in the wood. The hyphae secrete enzymes that dissolve the cellulose and lining in the wood, transforming them into simple chemicals that the fungi then use as food. In its incipient stages, decay is often invisible to the naked eye, but it is capable of completely destroying large volumes of wood. The termites, carpenter ants and other wood invading insects bore into the wood, thereby destroying its integrity and structural strength. The problem of invasion by pests is exacerbated by the cracking of wood upon drying. As wood dries to below about 30 percent moisture content, it shrinks. Since the moisture level of freshly-cut wood decreases with the distance from the center, as the wood dries, it produces V-shaped cracks, which expose additional surface for penetration by pests. Additionally, any protection of a wooden object which is limited to the outside surface of such object is rendered inoperative once cracks are formed.

The magnitude of the problem of decay of wood is illustrated with wooden utility poles. There are about 120 million wooden utility poles in service in the United States, of which 15 to 20 million are currently in need of treatment to remain in service, and 4 to 6 million more become defective each year. A survey by the Electric Power Research Institute ("EPRI") indicated that, on average, it costs $810 to replace an electric

distribution pole, and $1690 to replace an electric transmission pole.

The presently accepted commercial approach to protection of new utility poles involves pressure treatment of the outer layers of the lower portions of poles with various organic or inorganic compounds. One widely used preservative is creosote, produced by the destructive distillation of coal. Another organic preservative that has been commonly used to impregnate wooden objects, including utility poles, is pentachlorophenol ("penta"). However, its use in the United States has been severely restricted by the U.S. Environmental Protection Agency. Wooden poles are also impregnated with inorganic compounds, such as chromated copper arsenical (CCA), ammoniacal copper arsenate (ACA) or ammoniacal copper zinc arsenate (ACZA) compounds. A problem with these inorganic wood impregnants, however, is that they leach out and quickly lose their effectiveness in preserving the wood.

A more recent approach to overcoming decay of wooden utility poles is by placing a clamshell mold around the pole. The clamshell mold extends from about 2-3 feet above the soil surface to about 2-3 feet below the soil surface. A resin mixture is placed in an annulus between the clamshell mold and the utility pole wherein the resin fills cracks and is allowed to cure and harden. Upon removal of the clamshell mold, the cured resin supports the pole and retards further decay of the wood. A pesticide or insecticide may be injected with the resin. However, the effective lifetime of the pesticide in the resin is relatively short and is not easily renewed.

A problem common to treatment of wood by impregnation with either organic or inorganic preservatives is that the impregnants reach only the surface layers of the

wooden objects. Accordingly, wood cracking exposes untreated areas which are subject to decay.

The pressure impregnation approach provides limited decay protection for a few years up to generally about 15 years. Moreover, the pressure impregnation approach cannot be applied to wooden poles already in place. The decay protection of poles already in place may be extended by periodic inspection and treatment, as necessary, with the fumigants, such as chloropicrin (trichloronitromethane), VAPAM (sodium methyldithiocarbamate) a non-volatile solid which is hydrolyzed to form (methyl isocyanate) or VORLEX, a volatile liquid containing the bioactive ingredient of methyl isocyanate in conjunction with physical strengthening of the deteriorated pole. Such remedial treatment has been shown to arrest fungal activity in Douglas fir poles for up to 10 years. (See R.D. Graham et al., Controlling Biological Deterioration of Wood with Volatile Chemicals, EPRI Report EL-1480 (Oregon State University, 1980). The treatment with fumigants generally involves drilling a hole at ground level downward and toward the center of the pole and pouring of the fumigant into the hole. The physical strengthening of the deteriorated pole generally involves placing reinforcing structures, such as metal sheath, concrete poured jackets, or an adjacent supporting pole.

The problem with the current treatment and repair methods is that they are effective for relatively short periods of time and necessitate regular costly manpower-intensive inspections and continual further treatments and repairs. Providing an excess quantity of an impregnant or a fumigant does not solve the problem of the short duration of the protection. The excess of such impregnant of fumigant is rapidly lost to the air and soil decreasing the long-term effectiveness. Moreover,

losses of impregnants or fumigants may cause significant environmental problems. Also, additional impregnants and fumigants are subject to decomposition, which renders them ineffective in the long run and not cost effective in the short run. The concentration of bioactive ingredients resulting from a single application of an impregnant or fumigant starts out well above the minimum level necessary for effectiveness, but decreases rapidly with passing time, dropping quickly below the minimum effective level.

Since a long-term solution to pesticide intrusion is desired, the pesticide which is used to control such intrusion can be incorporated into a controlled release device. A "controlled release device" refers to a substance that results in controlled and sustained release of an bioactive chemical from its surface. The device provides a method for the controlled release of the chemical into the surrounding environment. The chemical released into the environment establishes an effective zone of action.

Presently, there are at least three controlled release packaging systems, including microcapsules, coated granules, and chemically-bound fungicides, wherein the fungicide is chemically bound to a polymer.

While there are a number of reasons for recommending microencapsulation (it is highly versatile, makes use of a variety of manufacturing techniques, and reduces the toxicity of the contained material), it is essentially a short-term system, with lifetimes measured in months rather than years. Additionally, microencapsulation can add significantly to the cost of the fungicide being encapsulated. Furthermore, this process has no use in protecting the other portions of the wood.

Coated granules have a pesticide absorbed onto a matrix such as clay and then coated with cross-linked

resins which helps slow the release rate. Clay loses or releases pesticide over a short period of at most a few weeks.

Chemically-bound pesticides are made by chemically binding the pesticide to a polymer, either by being reacting the pesticide with a preformed polymer, or by attaching the pesticide to a monomer and then cross linking to form the polymer. The amount of pesticide chemically bound in a polymer affects the integrity, strength and properties of the polymer. Accordingly, the amount of pesticide that is chemically bound is limited to less than about 10 wt% to maintain polymer integrity.

A Japanese patent J5 8039-601, JA-1983-03 describes an antibacterial agent placed in a hydrophillic polymer and formed into a stick or tablet that is inserted into a hole into the trunk of a tree. The hydrophillic polymer absorbs moisture from the tree and dissolves thereby releasing the antibacterial agent. This controlled release device would be inoperative in non-living dry wood. In fact, it would be inoperative in an environment of unsteady moisture exposure since overexposure to moisture would result in dissolution too quickly and under exposure to moisture would result in insufficient dissolution to release the antibacterial agent.

There is, therefore, a long felt and unsatisfied need for a device, a method and a system of preserving wooden objects for a prolonged period of time, and independent of moisture exposure by preventing decay and deterioration of such objects by pests such as fungi, termites, ants, and other wood invading flora and fauna. The need is particularly keen in connection with the prevention of decay and deterioration of wooden utility poles, railroad ties, fence posts, and buildings.

## SUMMARY OF THE INVENTION

This invention pertains both to protection of wooden objects in direct contact with soil from pest invasion, wooden objects including but not limited to wooden utility poles, wooden railroad ties and wooden fence posts.

The present invention provides a device, and a method for preventing, for a prolonged period of time, the decay and the deterioration of wooden objects caused by the invasion of pests such as fungi, termites, ants, and other wood invading flora and fauna (e.g. insects). The present invention is a bound friable mixture that may be placed in a polymer. A bound friable mixture is achieved by combining the bioactive chemical containing at least one fungicide with a binding carrier capable of binding the bioactive chemical therein or thereto. Binding is by sorption, e.g. adsorption, absorption, chemisorption and combinations thereof, and is characterized or distinguished from surface tension adhesion of a liquid to a solid surface by a greater retention or slower release of the bioactive chemical. The bound friable mixture may then be added to a prepolymer (monomer or powdered polymer) to form a controlled release device for deployment.

The resulting controlled release device is preferably in the form of a pellet or rod that is insertable into a hole in the wooden object, or in the form of a sheet that may be placed under or around a foundation. The device may be applied to the outside surface of the wood alone or in combination with an internally placed device. The controlled release device releases the pesticide at a predetermined rate to establish a biochemical barrier or exclusion zone to prevent invasion of pests for a predetermined period of time.

For devices releasing the pesticide outward from inside the wooden object, a minimum effective level is maintained throughout the object, thereby eliminating problems associated with cracking of the wood. Furthermore, such devices are capable of preventing environmental and health problems caused by the unduly high concentration of the pesticide at the surface of wooden objects or in the local environment around the object.

In a preferred embodiment, the pesticide and binding carrier are mixed first then placed into the pre-polymer.

In accordance with one aspect of the present invention, the device releases pesticide at a high rate initially and a lower, steady rate thereafter. This release profile assures that the wooden object becomes protected in a relatively short period of time, and that, subsequent to reaching the minimum effective level, only the amount of pesticide necessary to replace the degraded pesticide is released. This release profile diminishes potential environmental and health problems of the treatment and reduces the cost of the treatment.

In accordance with another aspect of the present invention, the device is applied to the outside surface of the wooden object in the form of a coat containing pesticide which is released in a controlled manner. The coat is applied to the external surface of the wooden object and maintains the minimum effective level of pesticide at the surface of the wood and/or in the surrounding soil.

In accordance with another aspect of this invention, a member which at least partially covers the surface outside is externally applied to the wood object. This member with reservoirs holding the controlled release device provides the minimum effective level of pesticide to protect the wood structure.

In accordance with the further object of the present invention, the device is placed inside the wooden object at about ground level allowing the pesticide to be carried laterally and longitudinally by molecular and gaseous diffusion and longitudinally primarily by the capillary action of the wood structure and moisture.

The present invention, together with the attendant objects and advantages, will best be understood with reference to the detailed description below read in conjunction with the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of the comparison of concentrations of a pesticide applied in a single dose and by the process and device of the present invention to a wooden object as a function of time.

FIG. 2 is a perspective view of a top section of a wooden telephone pole showing the location of the controlled release device constructed in accordance with the present invention.

FIG. 3 is a perspective view of a wooden telephone pole being treated by the process of the present invention to install a pesticide-releasing device of the present invention.

FIG. 4 is a perspective view of the wooden telephone pole of FIG. 3 showing an installed pesticide-releasing device constructed in accordance with the present invention.

FIG. 5 is a perspective view of drilling operation in the process of installation of the pesticide-releasing device of the present invention into new wooden utility poles, showing in partial cross-section the bore for the pesticide-releasing device of the present invention.

FIG. 6 is a perspective view of the railroad tracks mounted on railroad ties which contain the pesticide-releasing devices constructed and installed in accordance with the present invention.

FIG. 7 is a perspective view of the bottom of a wooden utility pole covered with a controlled pesticide release layer constructed in accordance with an embodiment of the present invention.

FIG. 8 is a perspective view of a railroad tie whose lower surface is covered with a controlled pesticide release layer constructed in accordance with an embodiment of the present invention.

FIG. 9 is a cross-sectional view of a wooden utility pole surrounded by a controlled-release device constructed in accordance with an embodiment of the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

It has been discovered that the longevity of a pest control can be greatly increased by first combining the bioactive chemical containing at least one fungicide, with a binding carrier as a bound friable mixture. A wood attacking pest controlled release device may then be formed by placing the bound friable mixture into a polymer. The polymer may be from a preform of a monomer or a polymer powder that is then formed into pellet, rod, strip, sheet or any suitable shape for the desired deployment of the wood attacking pest controlled release device.

Wood attacking pests include but are not limited to microorganisms for example fungi, and/or mold; macroorganisms including insects and arachnids, for example ants, termites, beetles, spiders; and combinations thereof.

Decay and deterioration of wooden objects maintained in soil, can be prevented for a prolonged period of time by a controlled release device which releases a pesticide at a predetermined rate into the wooden object to maintain at least a portion of such object above the pesticide concentration that can be tolerated by pesticides. The devices of the present invention can prevent pest infestation of wooden objects up to the expected lifetime of such objects. For example, the devices of the present invention can prevent pest caused decay and deterioration of wooden utility poles for at least twenty (20) years and preferably at least fifty (50) years.

The process of the present invention for treating wooden objects can be used on any wooden object; however, as a practical matter, it is mostly useful in treating wooden objects which are proximate soil either within soil, in contact with soil, or sufficiently near soil that pests have access to the wooden object(s). The wooden objects for which the present invention is especially useful include: wooden utility poles, wooden railroad ties, wooden bridge parts, such as bridge bracings, wooden fence posts, and the like. As it should be clear to one skilled in the art, the term "wooden objects" is used herein to refer to objects made of the wood, i.e., out of dead tree trunk and branches. The term "wooden objects" is not intended to refer to live trees.

The device of the present invention can be installed in wooden objects which are already in the soil and in those which have not yet been placed in the soil. The present invention is effective in treating both the wooden objects that have been infested by pests and those which have not yet suffered from pest infestation. Preferred deployment is for the device of the present

invention to be installed in the wooden object, then release the pesticide at a controlled rate into the wood. The device's pesticide-release rate is selected to maintain at least a portion of the wooden object at the minimum effective level. As used in the specification and the appended claims, the term "minimum effective level" is defined to be the pesticide level which can be tolerated by pests. In some applications, a creation of an exclusion zone which pests cannot penetrate is sufficient to protect the entire object. The creation of such a zone is advantageous in that less pesticide is required than if such a level was maintained throughout the whole object. Also, it often is much less expensive to install devices for creation of such zone than for treating the entire object. Finally, the creation of a pest barrier or exclusion zone is advantageous for ecological and human safety reasons. This is because most of the object does not contain a pesticide.

The controlled release devices of the present invention preferably have a release rate shown in FIG. 1, which is initially rapid so as to bring the pesticide concentration of the zone in the wooden object or the entire object to the desired concentration level as quickly as possible. Thereafter, the release rate is slower, preferably just sufficient to maintain the object or the selected zone of the wooden object above the minimum effective level to prevent pest infestation. The initial high release rate is achieved by allowing the pesticide to release from the matrix prior to inserting the device into or onto the wooden object. The amount of the released pesticide can be varied by the varying temperature and the amount of time for the release prior to inserting the device.

It has been found that hydrophobic polymers serve as effective pesticide release devices because they can act

as reservoirs and release regulating mechanisms for the pesticide. They are able to function in this manner because they trap the pesticide within their matrices and matrix acts as a reservoir for the pesticide. Moreover, these polymeric matrices can protect the pesticide from degradation. Thus, the polymeric delivery system is able to maintain an effective dose of the pesticide for a substantial length of time in a zone surrounding the device. Hydrophobicity of the pesticide containing polymer is preferably less than about 13 on either the HLB or solubility parameter scale. More preferred in a hydrophobicity less than about 10 and most preferably less than about 8. Specifically excluded are polymers that are water soluble, and/or have ionic groups (e.g. carboxylic acids, sulfonic acids), and/or have been treated with water to form materials that contain water. However, the present invention includes blends for example polyethylene and POLYOX wherein POLYOX is a water soluble ethylene oxide polymer. However, the bioactive pesticide is contained within the hydrophobic polymer.

The pesticides used in the present invention depend on the anticipated pests which in turn depend on many factors, including the type of wood, the geographical location of the wooden object, and the soil in which the object is maintained. In most cases, the pesticide is selected to eliminate fungi and wood boring insects. The wood boring insects which cause particular problems include carpenter ants and termites (soil born or dry wood). If a single pesticide does not eliminate all of the anticipated pests, the device can incorporate a combination of pesticides, as long as such pesticides are compatible with each other or one another. If the pesticides are not compatible because of different release rates, or, for other reasons, separate devices can be used for treatment in accordance with the present

invention. For termites and/or ants, the presently preferred pesticide is a pyrethrin, specifically for example tefluthrin, permethrin, cypermethrin, or combinations thereof. Other preferred pesticides include especially fenoxycarb, and chlorpyrifos, sold under the trademark Chlorophos by Dow Chemical.

For fungi, pesticides include but are not limited to tri-chloronitromethane under the tradename Chloropicrin, a mixture of methylisothiocyanate and 1-3 dichloropropane under the tradename Vorlex, sodium N-methyl dithiocarbomate under the tradename Vapam, 2,3,5,6 - tetracholoro - 1,9 - benzoquinone under the tradename Chloronil, calcium cyanamide, biphenyl, copper naphthenate, dichlorphen, fentin hydroxide and combinations thereof. Preferred fungicides are biphenyl, dichlorophen, and Chloropicrin, which are water soluble and incorporable into urethane or low density polyethylene. The amount of polymer is preferably about 70 wt% with fungicide in an amount from about 5 wt% to about 30 wt% and a binding carrier in an amount from about 5 wt% to about 30 wt%.

Other exemplary insecticides include but are not limited to isofenphos, fenvalerate, cypermethrin, permethrin, pyrethrin, fenoxycarb, tefluthrin, and combinations thereof, as well as in combination with any of the previously cited pesticides.

Polymer selection for the controlled release device depends upon the conditions encountered, either inside the pole, or on its outer surface. The polymer matrices must be able to endure the seasonal variations in temperature and moisture. Moreover, because of their naked exposure to the elements, the matrices used to coat the poles must be able to withstand amplified conditions. The polymer utilized in the coating must meet three requirements. First, it must be bound to the wood pole

so that it remains intact during handling. Second, it must provide an adequate diffusion barrier for the pesticide so that the release rate will be compatible with the desired service life. Finally, the selection of the polymer must account for the characteristics of the pesticide.

Polymers capable of withstanding such conditions and providing the desired release rates for the pesticides can be classified into four groups: thermoplastic polymers, thermoset polymers, elastomeric polymer and copolymers thereof. By way of example and not intending to limit the scope of this invention, low density polyethylene, high density polyethylene, vinyl acetate, urethane, polyester, silicone, neoprene, and isoprene polymer and co-polymer can all be used in this invention.

Where synthetic pyrethroids are used, high density polyethylene is the preferred polymer, specifically polyethylene MA778000. More specifically, pyrethroids having both low water solubility and low vapor pressures, the low vapor pressures in the range of 1 nPa to 100 mPa, including tefluthrin (80 mPa), permethrin (45 nPA), lambdacyhalthrin (200 nPa), resmethrin (1.5 nPa), deltamethrin (0.002 mPa), cypermethrin (0.5 nPa), cyphenothrin (0.12 mPa) and cyfluthrin (1 mPa) are preferred in combination with high density polyethylene. Most preferred are permethrin, cyphenothrin, tefluthrin, or combinations thereof because of their combination of efficacy and their release rates from or through a polymer. For more water soluble bioactive chemicals, urethane, specifically Urethane 2200, Hytrel polyesters, and low density polyethylene, specifically Microthene 763 are used. Water soluble bioactive chemicals include diazinon, chlorpyrifos, fenoxycarb, tralomethrin, methyl isothiocyanate and pentachlorophenol.

In addition, it is advantageous to add filler and/or binding carrier to optimize the loading of the polymer. The inclusion of such a substance allows greater amounts of pesticide to be loaded into the desired polymer, while, at the same time, assisting in the release rate of the polymer. Binding carrier includes carbon, hydroxyapatite, alumina, silicoalumina, and combinations thereof. Carbon may be in the form of activated carbon, carbon black, and combinations thereof. Carbon black is the preferred binding carrier. More specifically, Vulcan XC-72 is preferred because Vulcan XC-72 has greater adsorption capacity compared to other carbon blacks. For bioactive chemicals that are liquid at room temperature, for example diazinon (pesticide) and copper naphthanate (fungicide), hydroxyapatite is the preferred binding carrier.

For high density polyethylene, the preferred amount of high density polythene is about 70 wt% and low vapor pressure bioactive chemicals in an amount of about 10 wt%, with the binding carrier in an amount of about 20 wt%. For low density polyethylene, polyester, urethane the preferred amount of plastic is about 65 wt%, and water soluble bioactive chemicals of about 15 wt%, with the amount of carrier about 0 wt% to about 25 wt%. For all combinations, bioactive chemical may range from about 5 wt% to about 30 wt% and binding carrier from about 0 wt% to about 25 wt%.

When a binding carrier is added, it has been found that simply adding the binding carrier to a mix of pesticide and pre-polymer results in poor formability of the controlled release device and permits evaporation of the pesticide. Accordingly, it is preferred to first mix the pesticide into the binding carrier as a bound friable mixture so that the pesticide is preferably bound either onto the surface of the binding carrier or into the bulk

volume of the binding carrier or both. The bound friable mixture of pesticide and binding carrier is then added to a polymer. The bound pesticide is retarded or prevented from evaporation during subsequent forming of the polymer.

The pesticide is best mixed with carrier with the pesticide in a liquid form. Some pesticides are in liquid form at room temperature, and others are solid or near solid at room temperature. Accordingly, heating the pesticide may be necessary to insure a liquid form for mixing with the binding carrier. For a pesticide in solid form with a high melting temperature, for example the fungicide carbendazin, the solid form is preferably a powder or granular form mixed with the binding carrier. The pesticide may be in the form of a paste and mixed with a binding carrier.

In a further embodiment, the controlled release device is constructed in two parts, an inner part surrounded by an outer part. The inner part comprises a mix of pesticide and binding carrier with the outer part a hydrophobic polymer encapsulating the inner part. The outer part may also contain pesticide and binding carrier that is the same or different compared to the inner part.

The inner part preferably has about 60 wt% pesticide, 30 wt% binding carrier and 10 wt% polymer, and may range from about 5 wt% to about 70 wt% pesticide, 10 wt% to about 95 wt% binding carrier and 0 wt% to about 85 wt% polymer.

Forms of the controlled release device include sheets, rods, pellets, and two-part constructions including inner part and outer part rods or pellets, and/or multi-laminate sheets wherein one sheet contains the pesticide or pesticide and binding carrier and another sheet is added to prevent photodegradation of the pesticide from light exposure.

When the controlled release device is for insertion into the wooden object, the pesticide must be loaded into the polymer in sufficient amounts to maintain a "minimal effective level." It is preferred to maintain the concentration in parts by weight of the polymer from about 50 to about 80, the concentration of the pesticide from about 5 to about 30, and the concentration of the binding carrier from about 5 to about 20. By so loading the polymer, the minimum effective level can be maintained for at least seven (7) years. As the concentration profile shown in Fig. 1, a polymeric controlled release device can maintain a minimal effective level of pesticide for much greater periods of time than single application methods.

The devices of the present invention can have any physical shape. If the device is inserted inside the wooden object, it is desirable to have the device shaped to conform to the cavity. Sheets, sleeves, multiple layers, pellets, dots on geotextile, pots, pot covers, and strips are only a few of the shapes that may embody the present invention.

In some cases, it is desirable to incorporate the device into the wood in a liquid or in a gel form, which may or may not solidify once it is incorporated. For example, a pesticide can be incorporated into a molten polymer which can then be injected in a molten state into a cavity in the wooden object. The polymer then solidifies, creating a solid device which fits tightly in the cavity. Similarly, the pesticide in a molten polymer may be spread on a surface or wooden object and allowed to solidify, creating a device which surrounds a portion of the wooden object as illustrated in FIG. 3.

For utility poles, as illustrated in FIG.s 2-5, it is preferred to insert the device as a controlled release device near the center of the pole so that the pesticide

is carried outward by diffusion and longitudinally by the capillary action of the wood structure. Once inserted, the opening into the pole must be sealed (not shown in the drawings). Preferably, the seal utilized provides a diffusion barrier for the pesticide. Since the cavity in the wooden objects is often created by drilling a hole therein, the devices of the present invention are often tubular, as generally shown in FIG.s 2-4. The diameter of the tubular device may be any diameter from thread size to several feet, but is preferably from about 0.5 inch to about 2 inches. The length may be any length but is preferably a length that does not extend beyond the wooden object. For a device inserted longitudinally in a portion of a wooden pole to be placed below grade, it is preferred that the length of the device approximately match the distance of the wooden pole extending below grade.

FIG. 2 illustrates an embodiment of this invention. It illustrates the controlled release device 51 already inserted near the top of the utility pole 12.

FIG. 3 shows the process of treating an already existing utility pole 11. In this figure, the lower end of the pole 11 is being drilled by a workman using drill 40. A collar 30 is set about the pole 11 to stabilize it as the drill 40 is being pushed downwards into the pole 11. FIG. 4 illustrates the finished pole 11 of FIG. 3 with the controlled release device 50 inserted.

FIG. 5 illustrates the drilling operation of a new utility pole 10. A drill 20 is used to bore a hole 30 in the pole 10 to provide a reservoir for the controlled release device.

FIG. 6 shows railroad cross-ties 72, wherein it is preferred to insert the controlled release device 52 near the center of the tie 72. A preferred mode of application includes a mechanism capable of movement on

rails 90, inserting the controlled release device 52 into cross-ties 72. The mechanism may utilize a plurality of drills to bore holes into the cross-ties 72.

In another embodiment of this invention, the polymer is placed in contact with the external surface of the wood object. This embodiment provides immediate protection for the wood. The embodiment maintains a minimum effective level of pesticide at the surface of the wood and, if in contact with the soil, the surrounding soil. Preferably, the concentration in part by weight of the polymer ranges from about 50 to about 80, the concentration of the pesticide from about 50 to about 80, more preferably from about 10 to about 30, and the concentration of the binding carrier from about 10 to about 20. By so loading the polymer, the minimum effective level can be maintained for at least seven (7) years. However, it should be noted that these concentrations can be varied by the user according to the desired results.

FIG.s 7 and 8 describe a mode of providing external contact. A coat 60 is applied to pole 12 in FIG. 7. Similarly, a coat 61 is applied to the bottom of a railroad cross-tie 70. These coats 60, 61 are applied in order to protect the wood structures before the pesticide inserted into the core can diffuse through the wood to reach the outer surface of the wooden object. The coat is able to provide an immediate minimum effective level of pesticide. Depending upon the place of application, this minimum effective level of pesticide can also be instituted in the adjacent soil or structure. Both FIG. 7 and 8 show the wood (pole 11 or cross-tie 70) being in intimate contact with the surface soil 71.

In another embodiment (FIG. 9) for providing external contact, a protective outer layer of pesticide can be applied by using a member 110 with reservoirs 120 to hold

the controlled release device 53. The member 110 configured as a ring partially covers the wood object 130. The ring 110, as the applied coating, can be placed on the wood object according to user preference. The coating and ring embodiments of this invention have been shown by way of example and do not limit the scope of this invention.

The pesticide may permeate the wooden object by several mechanisms. First, if a polar, water soluble, pesticide is used and the wood contains enough moisture, the pesticide is carried by the capillary action of the wood structure. Second, the pesticide having vapor pressure of about 1 mm Hg at 25°C diffuse relatively quickly through the porous molecular wood structure through gaseous diffusion. Such pesticides diffuse through from the center to the periphery of a telephone pole in about 4 to 6 months. The pesticides having vapor pressure equal to or less than about 1 diffuse more slowly, and those having vapor pressure of less than about 0.1 mm Hg do not effectively diffuse through the wood.

As stated above, the controlled release device may be positioned externally and/or internally in a variety of locations with respect to the wooden structure. If placed above ground level, the pesticide is carried laterally and longitudinally by molecular and gaseous diffusion and longitudinally by the capillary action of the wood structure and moisture. If placed at or about at ground level, a minimum effective level can also be maintained in the soil or surface surrounding the wood structure.

Example 1

The following controlled release devices were made and tested to obtain their release rates (Table 1). The devices were made as follows. All devices, except for those employing S-113 urethane, were injection molded into a thin sheet about 1/8 inch thick. The device employing S-113 urethane was case, a method typically used for thermoset polymers. All thermoplastics were formulated using sufficient amount of carbon black to carry pesticides. All thermoplastic polymers were formulated with 10 percent pesticide, 3 or 7 percent carbon black to absorb liquid pesticide and 87 to 83 percent by weight of polymer. Specifically, devices made from thermoplastic polymers and deltamethrin and lambdacyhalothrin contained 3 percent of carbon black. The devices made from the remaining pesticides and thermoplastic polymers contained 7 percent of carbon black.

The devices made from S-113 urethane (a thermoset polymer) were made from a polymer mix containing 60% S-113, 40% castor oil, and 5% of TIPA catalyst by weight. The polymer mix comprised 90% of the total weight of the device. The pesticide, deltamethrin, comprised the remaining 10% of the device. No carbon black was used in this device. The polymer/pesticide mixture was cast into a 1/8 inch thick sheet and heated at about 60°C for about 40 to 60 minutes to cure the cast sheet.

One inch squares were then cut from the thin sheets that were injection molded or cast, and the squares were tested for release rates as shown in Table 1.

Table 1 - Release Rates for Pesticide/Polymer Combinations

| Pesticide | Polymer | Release Rate |
|---|---|---|
| Deltamethrin | S-113 urethane | 25.2 μg/cm2/day |
| | Aromatic 80A | 16.8 μg/cm2/day |
| | pellethane 2102-80A | 8.8 μg/cm2/day |
| | pellethane 2102-55D | 8.0 μg/cm2/day |
| | Alipmtic PS-49-100 | 7.2 μg/cm2/day |
| Cypermethrin | polyurethane 3100 | 0.4 μg/cm2/day |
| | polyurethane 2200 | 0.7 μg/cm2/day |
| | EVA 763 | 27.3 μg/cm2/day |
| | Polyethylene MA 778-000 | 4.6 μg/cm2/day |
| Lambdacyhalothrin | polyurethane 3100 | 0.7 μg/cm2/day |
| | polyurethane 2200 | 2.0 μg/cm2/day |
| | EVA 763 | 20.6 μg/cm2/day |
| | Polyethylene MA 778-000 | 5.2 μg/cm2/day |
| Tefluthrin | polyurethane 3100 | 6.4 μg/cm2/day |
| | polyurethane 2200 | 25.0 μg/cm2/day |
| | EVA 763 | 40.4 μg/cm2/day |
| | Polyethylene MA 778-000 | 27.0 μg/cm2/day |
| Permethrin | polyurethane 3100 | 1.4 μg/cm2/day |
| | polyurethane 2200 | 1.3 μg/cm2/day |
| | EVA 763 | 28.5 μg/cm2/day |
| | Polyethylene MA 778-000 | 4.0 μg/cm2/day |
| Dichlorophen | Polyethylene MA 778-000 | 6.2 μg/cm2/day |

Example 2

Controlled release devices in the form of sheets are made having 10 wt% pesticide, 10 wt% binding carrier and 80 wt% high density polyethylene (Polyethylene MA 778-000).

Longevity as a function of sheet thickness is shown in Table 2.

Table 2 - Release Rate and Longevity as a Function of Sheet Thickness and Temperature

| Pesticide | Sheet Thickness (mil) | Release Rate ($\mu g/cm^2/day$) @ 23 °C | Longevity (years) @ 23 °C | Longevity (years) @ 35 °C |
|---|---|---|---|---|
| Permethrin | 60 | 1.5 | 8.6 | 3.2 |
| | 120 | | 17 | 6.5 |
| | 240 | | 35 | 13 |
| Tefluthrin | 60 | 1.3 | 9.1 | 3.1 |
| | 120 | | 18.2 | 5.9 |
| | 240 | | 39 | 10.4 |
| Diazinon | 60 | 11.7 | 1.1 | 0.6 |
| | 120 | | 2.3 | 1.3 |
| | 240 | | 4.8 | 2.7 |
| Biphenyl | 60 | 3.5 | 2.5 | 2.1 |
| | 120 | | 5.1 | 4.4 |
| | 240 | | 11.2 | 9.1 |
| Dichlorophen | 60 | 6.2 | 1.6 | 1.4 |
| | 120 | | 3.3 | 3.0 |
| | 240 | | 6.8 | 6.4 |

Release rates are substantially decreased compared to those in Tables 1 and 2 by an additional layer, for example metallized Mylar or Saran that is added to prevent photodegradation.

Example 3

A device having an inner part surrounded by or encapsulated by an outer part is constructed having an

overall mass of about 100g. The inner part contains 60 wt% pesticide and 40 wt% binding carrier. The outer part is high density polyethylene of a thickness of 120 mil. Release rates are shown in Table 3.

Table 3 - Release Rate for Encapsulated Two-Part Construction

| Pesticide | Release Rate ($\mu g/cm^2/day$) @ 23 °C | Longevity (years) @ 23 °C | Longevity (years) @ 35 °C |
|---|---|---|---|
| Permethrin | 16 | 68 | 38 |
| Tefluthrin | 31 | 35 | 18 |
| Diazinon | 28 | 39 | 24 |
| Biphenyl | 35 | 31 | 23 |
| Dichlorophen | 24 | 56 | 28 |

Example 4

A pellet is made having a mass of about 100g and a surface area of about 150 $cm^2$. The polymer is 70 wt% high density polyethylene, with 20 wt% pesticide and 10 wt% binding carrier. Release rates are shown in Table 4. Comparing Table 4 to Table 3, it is evident that the encapsulated two-part construction provides longer life than the pellet.

Table 4 - Release Rates From Pellet

| Pesticide | Release Rate ($\mu g/cm^2/day$) @ 23 °C | Longevity (years) @ 23 °C | Longevity (years) @ 35 °C |
|---|---|---|---|
| Permethrin | 12 | 30 | 14 |
| Tefluthrin | 11 | 33 | 16 |
| Diazinon | 45 | 8.1 | 5.1 |
| Biphenyl | 16 | 22 | 11 |
| Dichlorophen | 11 | 33 | 16 |

EXAMPLE 5

An experiment was conducted to demonstrate the effect of a binding carrier on release rate. The bioactive chemicals were tefluthrin and lambdacyhalothrin in an amount of 5 wt%, the binding carrier was carbon black in amounts of 0 wt% and 10 wt%, with the balance high density polyethylene (MA 778-000). Release rates were measured at 6 weeks after fabrication wherein samples were wiped weekly to remove surface accumulation of released bioactive chemical.

Results are shown in Table 5.

TABLE 5 - Release Rates for 0 wt% and 10 wt% Carbon Black

| Bioactive Chemical | Carbon Black (wt%) | Release Rate ($\mu g/cm^2/day$) |
|---|---|---|
| tefluthrin | 0 | 3.13 |
| tefluthrin | 10 | 0.71 |
| lambdacyhalothrin | 0 | 1.78 |
| " | 10 | 0.81 |
| " | 20 | 0.61 |

Closure

It should be apparent that a wide range of changes and modifications can be made to the embodiments described above. It is, therefore, intended that the foregoing description be regarded as illustrative rather than limiting, and that it be understood that it is the following claims, including all equivalents, which are intended to define this invention.

CLAIMS

We claim:

1. A bound friable mixture, comprising:

(a) an bioactive chemical; bound with

(b) a binding carrier selected from the group consisting of carbon black, activated carbon, alumina, hydroxyapatite, silicoalumina and combinations thereof.

2. A controlled release device for deterring a wood attacking pest, comprising:

(a) the bound friable mixture as recited in claim 1; within

(b) a polymer.

3. The controlled release device as recited in claim 2, wherein said bioactive chemical has a vapor pressure greater than about 0.1 mm Hg at 25 °C.

4. The controlled release device as recited in claim 2, wherein said polymer is in an amount from about 50 to about 90 parts by weight and said bound friable mixture is in an amount from about 10 to about 50 weight percent, providing a release rate of bioactive chemical from about 0.4 $\mu g/cm^2/day$ to about 40 $\mu g/cm^2/day$.

5. The controlled release device as recited in claim 1, wherein said bioactive chemical is a pesticide containing at least one fungicide

6. The controlled release device as recited in claim 5, wherein said fungicide is selected from the group consisting of tri-chloronitromethane, methylisothiocyanate and 1-3 dichloropropane, sodium N-

methyl dithiocarbomate, 2,3,5,6-tetracholoro-1,9-benzoquinone, calcium cyanamide, biphenyl, copper naphthenate, dichlorphen, fentin hydroxide and combinations thereof.

7. The controlled release device as recited in claim 2, wherein said binding carrier is selected from the group of carbon black, activated carbon and combinations thereof.

8. The controlled release device as recited in claim 2, wherein said binding carrier is in an amount from about 10 to about 20 parts by weight.

9. The controlled release device as recited in claim 2, wherein said polymer is hydrophobic.

10. The controlled release device as recited in claim 2, wherein said bound friable mixture is enveloped within said polymer.

11. The controlled release device as recited in claim 10, wherein enveloped is an encapsulation or surrounding of said bound friable mixture as an inner part with said hydrophobic polymer as an outer part.

12. The controlled release device as recited in claim 11, wherein enveloped is integration of said bound friable mixture within said hydrophobic polymer as the hydrophobic polymer is cross linked or cured.

13. The controlled release device as recited in claim 12, in the form of a rod, pellet, strip or sheet.

14. The controlled release device as recited in claim 13, wherein said sheet further comprises a second sheet for retarding or preventing photodegradation of said pesticide.

15. The controlled release device as recited in claim 14, wherein said second sheet is a polymer selected from the group consisting of metallized Mylar, saran, or combinations thereof.

16. The controlled release device as recited in claim 1, wherein said bioactive chemical is a pesticide.

17. The controlled release device as recited in claim 1, wherein said pesticide is selected from the group consisting of pyrethroid, isofenphos, fenvalerate, water soluble bioactive chemical and combinations thereof.

18. The controlled release device as recited in claim 17, wherein said pyrethroid is selected from the group consisting of tefluthrin, permethrin, lambdacyhalothrin, resmethrin, deltamethrin, cypermethrin, cyphenothrin, cyfluthrin, and combinations thereof.

19. A method of making a controlled release device useful for retarding or preventing decay or deterioration of a wooden object from a wood attacking pest, the method having the steps of:

(a) mixing a fungicide, with a binding carrier wherein the fungicide is bound to the binding carrier in a bound friable mix, then

(b) combining the bound friable mix with a polymer.

20. The method as recited in claim 19, wherein the pesticide is in a liquid form.

21. The method as recited in claim 19, wherein said combining is by mixing the bound friable mix with a pre-polymer thereby forming said hydrophobic polymer upon polymerization or curing.

22. The method as recited in claim 19, wherein said combining is by encasing said bound friable mix as an inner part with an outer part of said hydrophobic polymer.

23. The method as recited in claim 19, wherein said polymer is a hydrophobic polymer.

24. The method as recited in claim 23, wherein said hydrophobic polymer is selected from the group consisting of thermoplastic polymers, thermoset polymers, elastomeric polymer and copolymers thereof.

25. The method as recited in claim 23, wherein said hydrophobic polymer is selected from the group consisting of low density polyethylene, high density polyethylene vinyl acetate, urethane, polyester, silicone, neoprene, disoprene and combinations thereof.

26. The method as recited in claim 19, wherein said fungicide has a low vapor pressure.

27. The method as recited in claim 19, wherein said low vapor pressure pesticide is combined with a high density pre-polymer.

28. The method as recited in claim 27, wherein said high density pre-polymer is selected from the group consisting of high density polyethylene.

29. The method as recited in claim 19, wherein said fungicide is water soluble.

30. The method as recited in claim 29, wherein said fungicide is combined with a low density pre-polymer.

31. The method as recited in claim 29, wherein said low density pre-polymer is selected from the group consisting of urethane, polyester, low density polyethylene, and combinations thereof.

32. The method as recited in claim 19, wherein said fungicide is selected from the group consisting of trichloronitromethane under the tradename Chloropicrin, a mixture of methylisothiocyanate and 1-3 dichloropropane under the tradename Vorlex, sodium N-methyl dithiocarbomate under the tradename Vapam, 2,3,5,6 - tetracholoro - 1,9 - benzoquinone under the tradename Chloronil, calcium cyanamide, biphenyl, copper naphthenate, dichlorphen, fentin hydroxide and combinations thereof.

33. The method as recited in claim 19, wherein said a fungicide is selected from the group consisting of byphenyl, dichlorphen, Chlorpicrin, and combinations thereof.

34. The method as recited in claim 19, wherein said binding carrier is dried prior to mixing with said bioactive chemical.

35. A method of preventing or retarding decay and deterioration of a wooden object from wood attacking pests, comprising the steps of:

(a) making the controlled release device as recited in claim 15 with a release rate of at least about 0.4 $\mu g/cm^2/day$;

(b) creating a cavity in the wooden object;

(c) inserting the controlled release device into the cavity and closing the cavity; and

(d) permitting the pesticide to vaporize from a surface of said controlled release device and to diffuse into the molecular wood structure of the wooden object thereby creating an exclusion zone within the wooden object having a concentration of the pesticide above a minimum effective concentration preventing pest invasion into said exclusion zone.

36. A method of preventing the decay and deterioration of wooden objects in contact with soil caused by the invasion of pests comprising the steps of:

(a) mixing a pesticide including at least one fungicide, said pesticide in liquid form, with

(b) a binding carrier forming a bound friable mix,

(c) combining the bound friable mix with a polymer thereby forming a controlled release device, the concentration of the pesticide being sufficient to provide a predetermined release rate through said polymer and sufficient to provide a minimal effective level to prevent pest intrusion for a predetermined period of time; and

(d) placing the controlled release device proximate the wooden object.

37. The method of claim 36 wherein the controlled release device releases pesticide at an initially high rate and a lower, steady state rate thereafter.

38. The method of claim 36 wherein the minimal effective level is maintained throughout the whole wooden structure.

39. The method of claim 36 wherein the minimal effective level is maintained in a zone of the wooden structure.

40. The method of claim 36 where the polymer is selected from the group consisting of thermoset polymers, thermoplastic polymers, elastomeric polymers, thermoplastic polymers, elastomeric polymers, and copolymers thereof.

41. The method as recited in claim 36, wherein proximate is within said wooden object.

42. The method as recited in claim 36, wherein proximate is on an exterior surface of said wooden object.

43. The method as recited in claim 36, wherein proximate is touching or in physical contact with said wooden object.

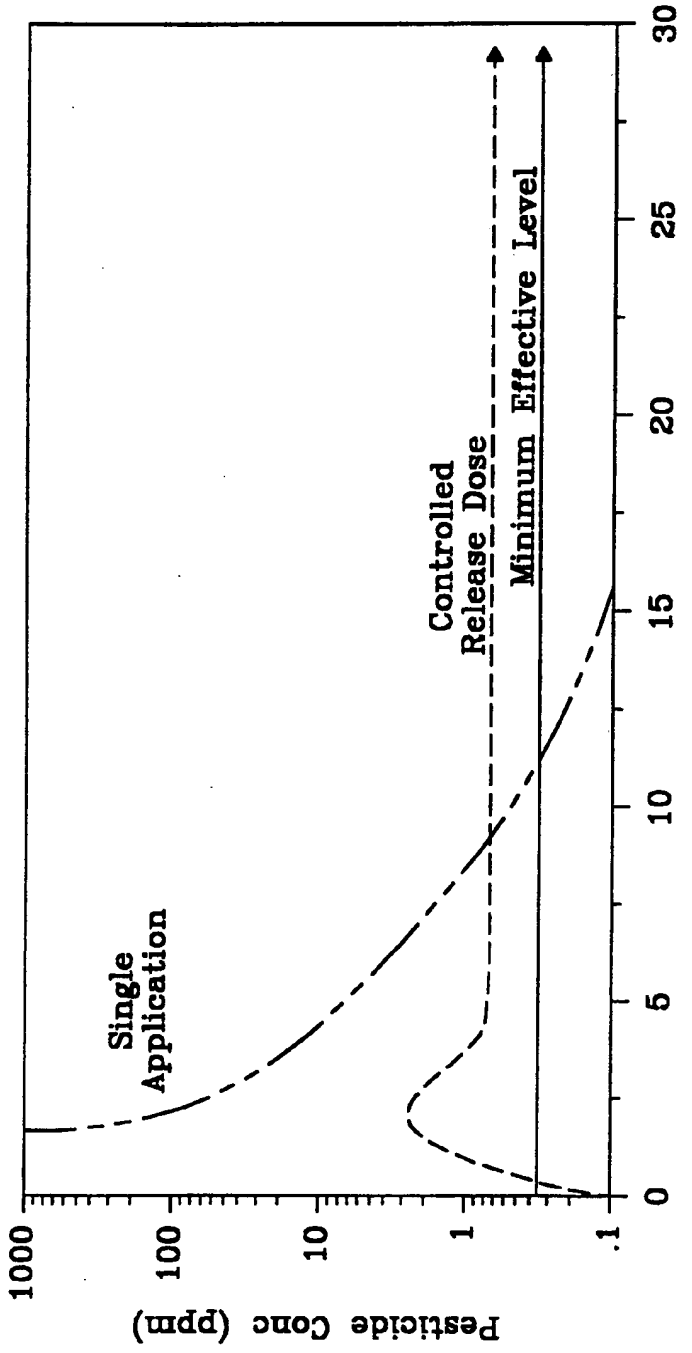
Pesticide Conc (ppm)
1000
100
10
1
.1
0
5
10
15
20
25
30
Time (years)
Single Application
Controlled Release Dose
Minimum Effective Level

*Fig. 1*

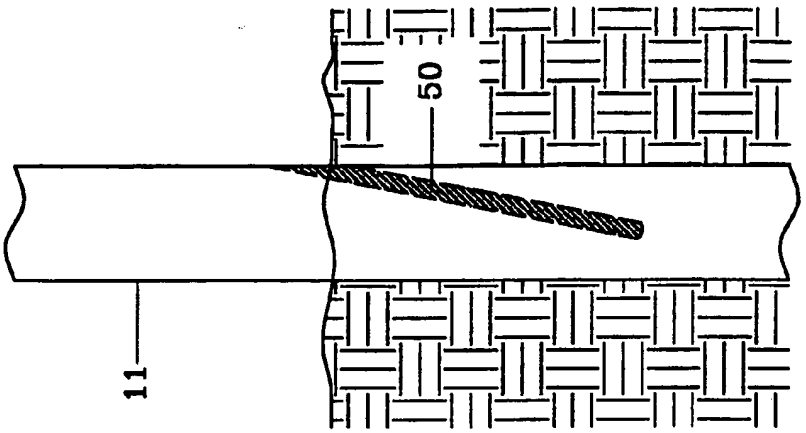


Fig. 4

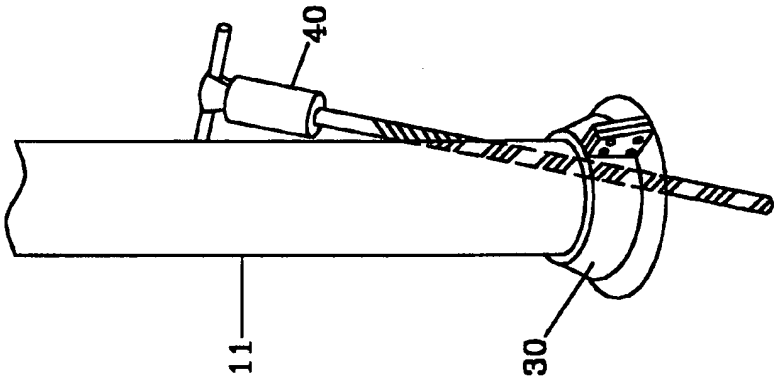


Fig. 3

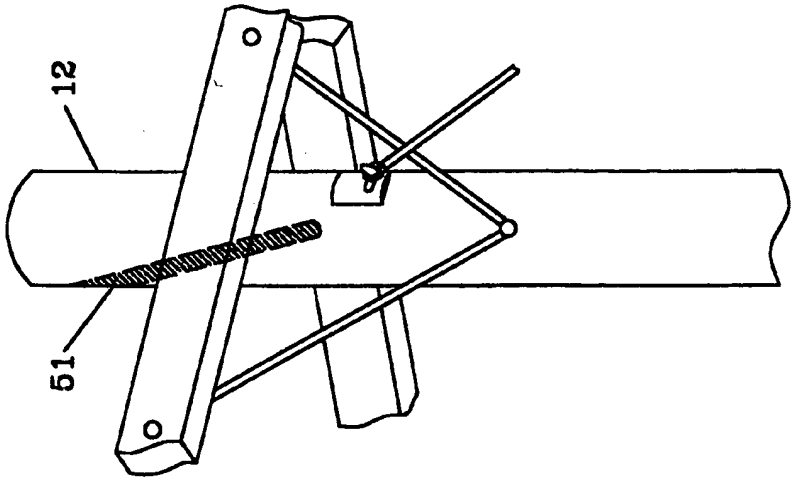


Fig. 2

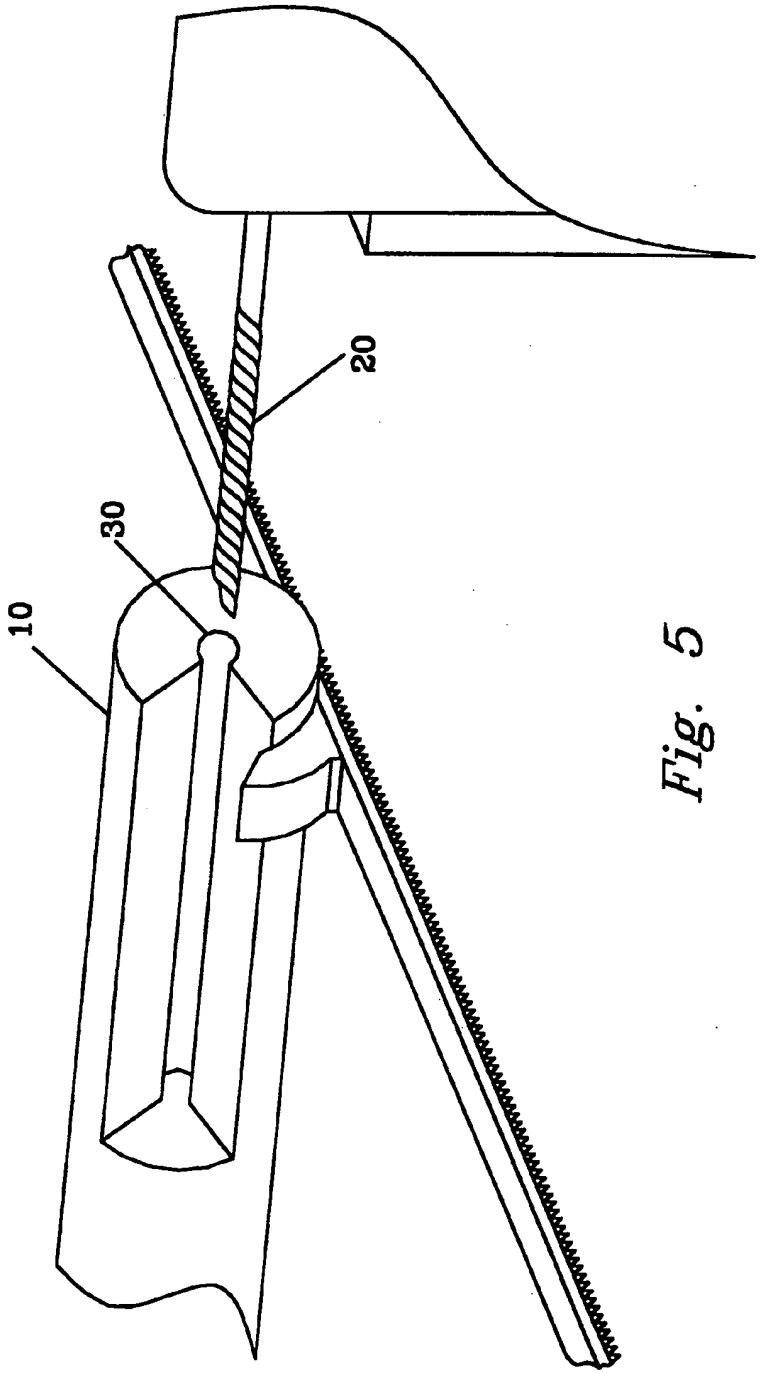


Fig. 5

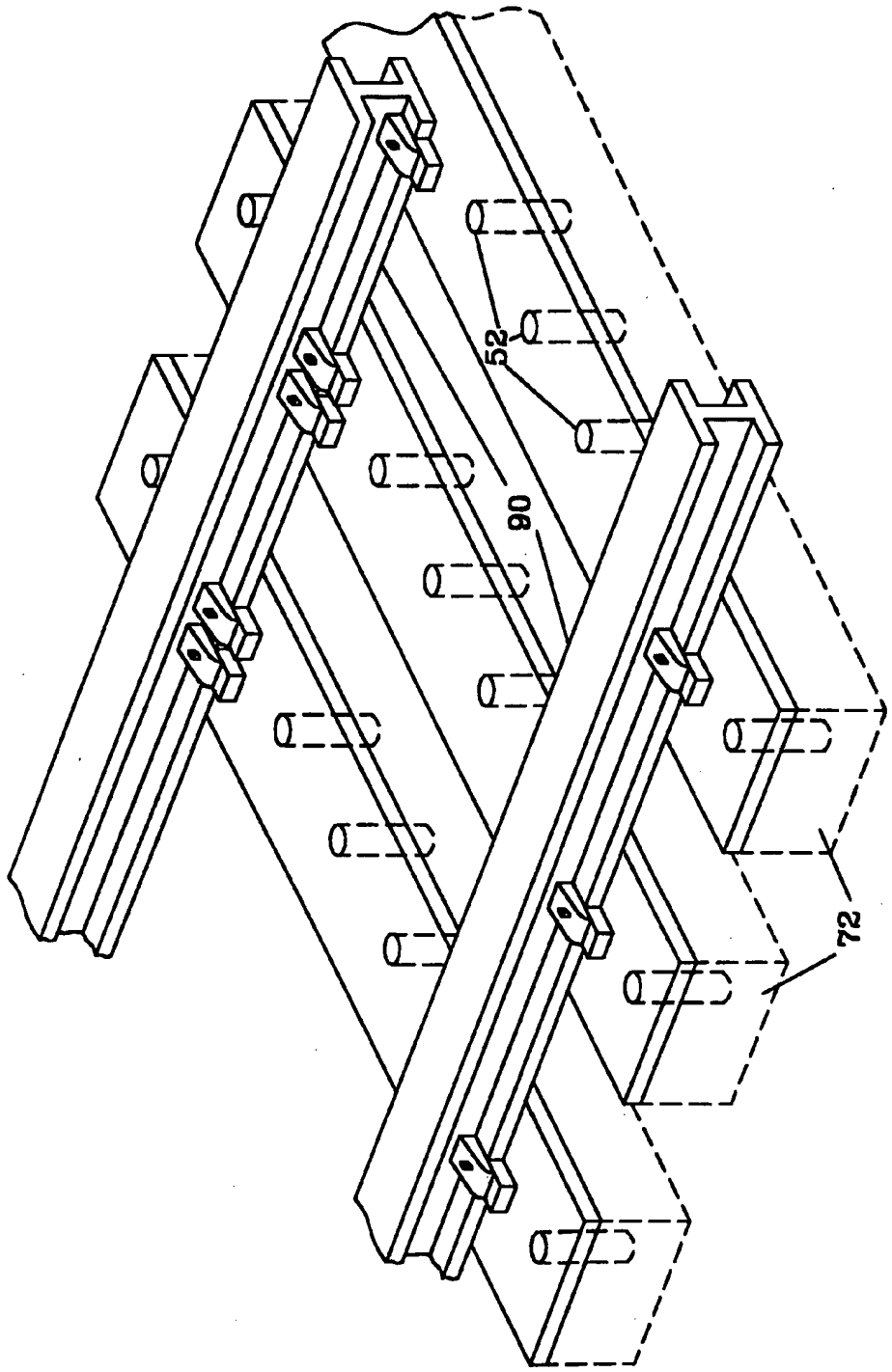


Fig. 6

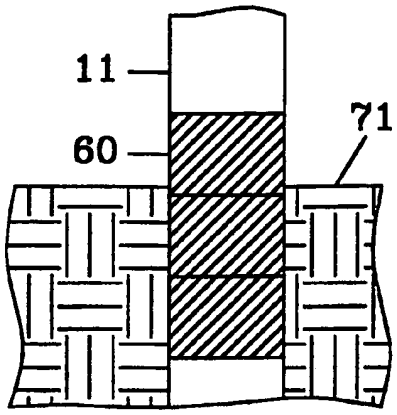


Fig. 7

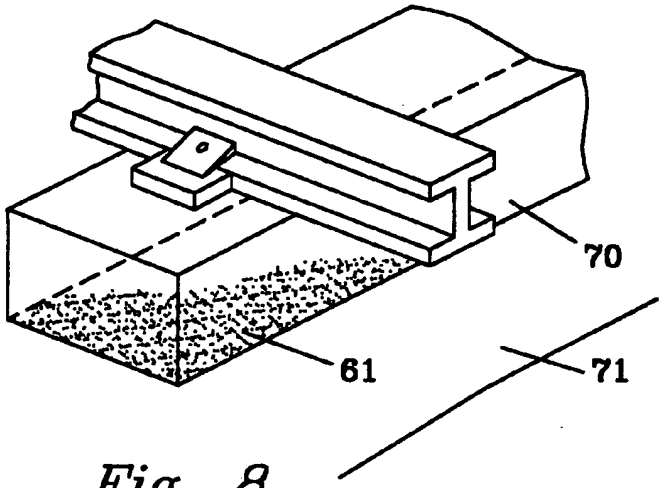


Fig. 8

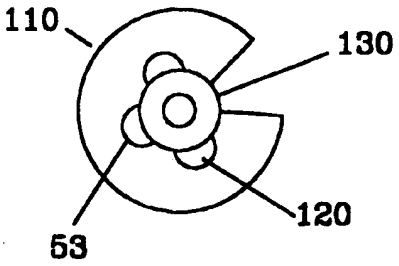


Fig. 9

# INTERNATIONAL SEARCH REPORT

Int :tional Application No
PCT/US 98/03265

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B27K3/02

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B27K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| Y | EP 0 152 976 A (TNO) 28 August 1985<br>see page 6, line 22-25; claims<br>--- | 35-43 |
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 3 November 1998 | 12/11/1998 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Dalkafouki, A |

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Int ional Application No
PCT/US 98/03265

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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